

A Tetranuclear Cuprous Halide Cluster Exhibiting Efficient Blue Thermally Activated Delayed Fluorescence^①

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ABSTRACT A new tetranuclear cuprous halide complex, (CuBr)₄(PN)₂ (PN = 2-(diphenylphosphaneyl)-6-methoxyppyridine), was synthesized and fully characterized. In solid state, this complex exhibits efficient blue emission with a photoluminescence quantum yield of 43.3% and a decay time of 19 μs at room temperature. The theoretical calculations, combined with the temperature dependence of spectroscopic properties and emission decay behaviors, indicate that the emission in the solid state originates from the ^{1,3}(MLCT + XLCT) excited states, which are in thermal equilibrium with a small energy gap of about 0.1 eV.

Keywords: cuprous complex, thermally activated delayed fluorescence, blue emission, photoluminescence;
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1 INTRODUCTION

Cuprous complexes have recently emerged as promising inexpensive alternatives for iridium complexes in electroluminescent applications because of their rich structural and photophysical properties^[1], as well as their thermally activated delayed fluorescence (TADF) mechanism^[2-4], which can harness both triplet and singlet excitons via efficient reverse intersystem crossing. Due to the low oxidation potential of the Cu⁺ ion, the emissive states of cuprous complexes usually exhibit significant metal-to-ligand charge transfer (MLCT) characteristic, endowing a narrow energy gap between the emissive states (¹MLCT and ³MLCT) and in turn ensuring efficient TADF emission at room temperature^[5].

Whereas, at the same time, the low oxidation potential of the Cu⁺ ion would cause these emissive MLCT states too low in energy to realized blue emission^[6].

The diverse coordination modes of Cu⁺ ion stimulate the search for emissive cuprous complexes with various structural features, amongst which cuprous halide clusters are a promising type of photoluminescent and electroluminescent materials due to their distinctive advantages^[7]. First, most of cuprous halide clusters are neutral and sublimable, and hence, are conducive to construct multilayer optoelectronic device^[8, 9]. Second, due to the presence of heavy halide atoms (Br or I), these complexes generally show efficient spin-orbit coupling (SOC)^[7, 10, 11], which play a crucial role in accelerating the intersystem crossing process and enhancing

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luminous efficiency. Herein, we report a novel tetranuclear cuprous complex, $(\text{CuBr})_4(\text{PN})_2$ (PN = 2-(diphenylphosphanyl)-6-methoxypyridine), which emits blue TADF at ambient temperature with a photoluminescence quantum yield of 43.3% and a decay time of 19 μs . The crystal structures, photophysical properties, and theoretical calculations have been systematically studied.

2 EXPERIMENTAL

2.1 Materials and methods

The ligand and other chemicals were purchased from commercial sources and used without further purification. ^1H NMR spectra were recorded on a Bruker Avance III 500MHz NMR spectrometer. Elemental analyses (C, H, N) were carried out with an Elemental Vario EL III elemental analyzer. The PL quantum yields, which were defined as the number of photons emitted per photon absorbed by the system, were measured by FluoroMax-4 equipped with an integrating sphere. Photoluminescence spectra and decay time were recorded on an Edinburgh Instruments FLS980 spectrometer using Xenon Lamp or OPO laser as the excitation light source. The variable-temperature measurements (77~313 K) of emission decay time and spectra were performed using a LINKAM THMS600 system with a range of 77~873 K. X-ray structure determination was carried out on the Bruker D8 Venture at 200 K.

2.2 Synthesis of $(\text{CuBr})_4(\text{PN})_2$

The complex was prepared according to the following procedure: A certain amount of CuBr (143 mg, 1 mmol) was dissolved into CH_3CN (2 mL), and then the mixture was poured into a solution of the PN ligand (293 mg, 1 mmol) in CH_2Cl_2 (2 mL). After stirring at room temperature for 1 hour, the reaction mixture was filtered. Single crystals of the cuprous complex suitable for X-ray diffraction measurement were obtained by slow diffusion of ether into the resulting filtrate. ^1H NMR (500 MHz, CD_2Cl_2) δ 8.53 (*s*, 4H), 8.10~6.91 (*m*, 22H), 3.76 (*s*, 6H). Elemental Analysis (%) Calcd. for $\text{C}_{36}\text{H}_{32}\text{Br}_4\text{Cu}_4\text{N}_2\text{O}_2\text{P}_2$: C, 37.26; H, 2.78; N, 2.41. Found: C, 37.32; H, 2.82; N, 2.45.

2.3 X-ray structure determination

A pale green crystal of the complex with dimensions of 0.28mm \times 0.19mm \times 0.15mm was used for X-ray diffraction analysis. The diffraction data were collected on a MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 49199 reflections were collected at 200 K in the range of $4.85 \leq 2\theta \leq 59.21^\circ$ by using an ω -scan mode, of which 5413 were unique with $R_{\text{int}} = 0.0279$ and 3735 were observed with $I > 2\sigma(I)$. The structures were solved by direct methods and refined by full-matrix least squares methods using the SHELXL-13 program package. All non-hydrogen atoms were refined with anisotropic thermal parameters. Selected bond lengths and bond angles of $(\text{CuBr})_4(\text{PN})_2$ are listed in Table 1.

Table 1. Selected Bond Lengths (\AA) and Bond Angles ($^\circ$) of $(\text{CuBr})_4(\text{PN})_2$

Bond	Dist.	Bond	Dist.	Angle	($^\circ$)	Angle	($^\circ$)
Br(1)–Cu(1)	2.396(7)	Cu(1)–Cu(2)	2.686(9)	Br(1)–Cu(1)–Br(2)	104.44(3)	P(1)–Cu(1)–Cu(2)	84.34(4)
Br(1)–Cu(2 ¹)	2.491(8)	Cu(1)–P(1)	2.188(12)	Br(1)–Cu(1)–Cu(2)	135.72(3)	Br(1 ¹)–Cu(2)–Br(2)	95.87(3)
Br(2)–Cu(1)	2.473(7)	Cu(2)–N(1)	1.987(3)	Br(2)–Cu(1)–Cu(2)	63.16(2)	N(1)–Cu(2)–Br(2)	122.29(10)
Br(2)–Cu(2 ¹)	2.529(8)			P(1)–Cu(1)–Br(1)	127.58(4)	N(1)–Cu(2)–Cu(1)	96.21(11)
Br(2)–Cu(2)	2.708(9)			P(1)–Cu(1)–Br(2)	126.38(4)	Cu(1)–Cu(2)–Br(2)	54.58(2)
Cu(1)–Cu(2 ¹)	2.691(8)			Cu(2)–Cu(1)–Cu(2 ¹)	81.70(3)	Cu(1)–Cu(2)–Cu(1 ¹)	98.30(3)

¹1 – x, 1 – y, 2 – z

2.4 Computational methodology

The density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed based on X-ray single-crystal structure at the hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) functional level^[3, 12]. The input data came from X-ray crystal structure. In this calculation, a “double- ζ ” quality basis set composed of Hay and Wadt’s effective core potentials (LANL2DZ) was employed for the Cu and Br atoms, and all-electron basis set

of 6-31G* was used for P, O, N, C, and H atoms. All calculations were carried out using Gaussian 09^[13]. The optimized structure and the visualization of frontier molecular orbitals were carried out through GaussView 5^[13]. The partition orbital composition was analyzed by using the Multiwfn 3.7 program^[14].

3 RESULTS AND DISCUSSION

The crystal structure of $(\text{CuBr})_4(\text{PN})_2$ was determined by

single-crystal X-ray diffraction analysis. The molecular structure drawing and the ORTEP diagram is shown in Fig. 1. The four copper atoms are arrayed in a parallelogram with two obtuse angles of 98.30° and two acute angles of 81.70° . The adjacent sides of the parallelogram exhibit unequal lengths of 2.686 and 2.691 Å, respectively, which are both shorter than twice the van der Waals radius of copper atom (2.8 Å), indicating significant metallophilic interactions between each two copper atoms. Each Cu_3 array which makes the acute angles in the parallelogram is μ^3 -capped with a bromine atom. The other two bromine atoms form μ^2 -bonds on each long side of the Cu_4 parallelogram. The two copper atoms on each short side of the parallelogram are chelated by a PN ligand in a C_2 -symmetric arrangement. The steric hindrance of methoxy group may play a key role in forming

the Cu_4Br_4 cluster. Yersin et al have synthesized cuprous complexes with Cu_2X_2 ($\text{X} = \text{Cl}, \text{Br}$ or I) core by using a similar PN ligand without any substituents on the pyridine ring or benzene ring^[11] (see Supporting Information for detail).

UV-vis absorption spectra of $(\text{CuBr})_4(\text{PN})_2$ and the PN ligand in CH_2Cl_2 are shown in Fig. 2. The strong absorption bands below 300 nm are assigned to $\pi\text{-}\pi^*$ transition^[6, 15]. And the weak absorption bands above 300 nm are assigned to $n\text{-}\pi^*$ transition. In addition, the absorption bands of $(\text{CuBr})_4(\text{PN})_2$ around 350 nm can be assigned to halide-to-ligand charge transfer (XLCT) and metal-to-ligand charge transfer (MLCT) according to the results of DFT and TD-DFT calculations.

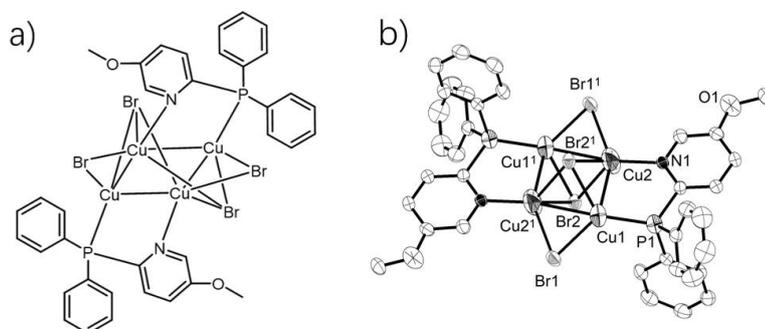


Fig. 1. Molecular structure (a) and ORTEP diagram (b) of the complex $(\text{CuBr})_4(\text{PN})_2$

DFT and TDDFT calculations were carried out to investigate the molecular orbitals and electronic states of the presented cuprous complex. The major contributions of the lowest excited singlet state (S_1) and the lowest excited triplet state (T_1) involve charge transfer transitions from the highest occupied molecular orbital (HOMO) and HOMO-2 to the lowest unoccupied molecular orbital (LUMO) and LUMO+1. As shown in Fig. 3, the HOMO and HOMO-2 of

$(\text{CuBr})_4(\text{PN})_2$ are mainly localized on the Cu_4Br_4 cluster, while the LUMO and LUMO+1 are almost entirely distributed over the pyridine rings on the NP ligands. Therefore, as summarized in Table 2, the low-lying transitions are characterized as metal-to-ligand charge transfer (MLCT) transitions mixed with halogen-to-ligand charge transfer (XLCT) transitions.

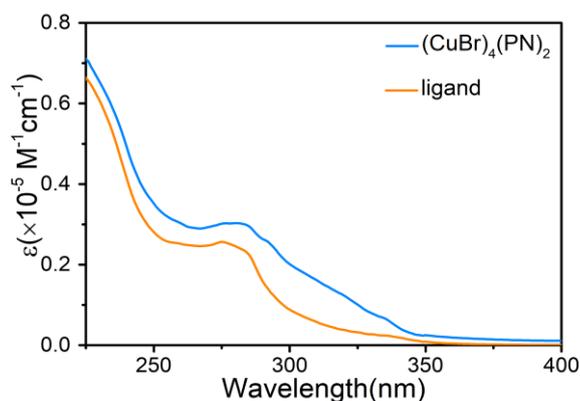


Fig. 2. UV-vis absorption spectra of $(\text{CuBr})_4(\text{PN})_2$ and the PN ligand

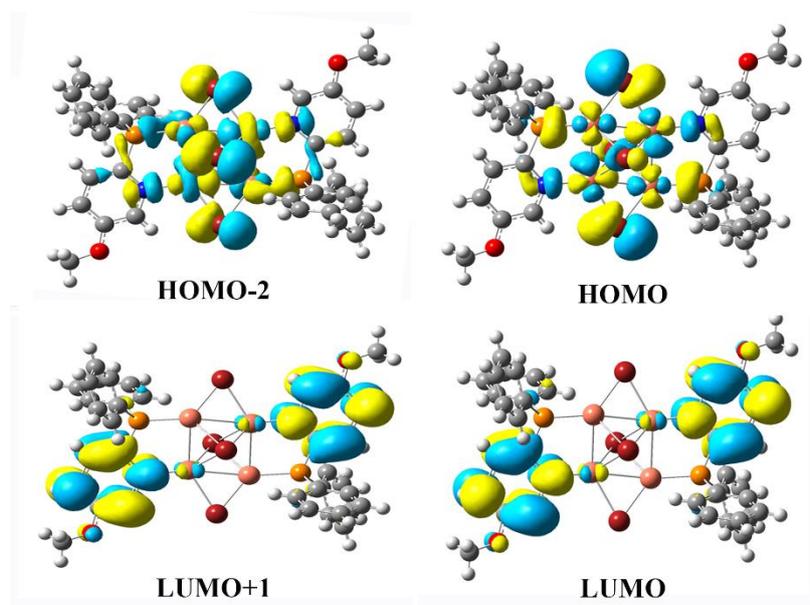


Fig. 3. HOMO, HOMO-2, LUMO, and LUMO+1 of $(\text{CuBr})_4(\text{PN})_2$ in the optimized ground state structure

Table 2. Transition Contribution of the Lowest Excited States

Energy state	Energy (eV)	Transition contribution (%)
S_1	2.600	$H \rightarrow L(66.77\%)$, $H-2 \rightarrow L+1(21.91\%)$, $H-1 \rightarrow L+1(5.02\%)$
T_1	2.509	$H \rightarrow L(71.11\%)$, $H-2 \rightarrow L+1(13.75\%)$, $H-1 \rightarrow L+1(11.84\%)$

The emission spectra and transient photoluminescence (PL) decay spectra of the investigated cuprous complex in solid state at 298 and 77 K are shown in Figs. 4 and 5. This complex exhibits blue emission with a spectral maximum of 488 nm with a photoluminescence quantum yield of 43.3% when excited at room temperature. As compared to the reported binuclear cuprous complexes based on the similar NP ligand and bromine ion, the emission spectrum peak of $(\text{CuBr})_4(\text{PN})_2$ blue shift by 13 nm (see Supporting Information for detail comparison). Considering the dominant (M+X)LCT transition characteristics of the lowest excited states as revealed by the calculation results, such emission blue-shift should be attributed to the weakened electron-withdrawing ability of the PN ligand by methoxy

substituent. This result indicates that it should be a promising strategy to obtain blue-emitting cuprous complexes by introducing electron-donating group into the ligand to destabilize the LUMO level. As the temperature decreases from 300 to 77 K, the emission spectrum peak red shifts from 488 to 503 nm accompanied with the decay time increase from 19 to 37.6 μs . The temperature dependence of spectroscopic properties and emission decay behaviors reveal the presence of two thermally equilibrated emissive states, namely S_1 and T_1 . To further investigate the behaviors of the two excited states, decay time at different temperature ranging from 77 to 298 K was measured and summarized in Fig. 6. The observed overall decay time τ can be expressed by the following Boltzmann-type equation:

$$\tau_{obs} = \frac{1 + \frac{1}{3} \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right)}{\frac{1}{\tau(T_1)} + \frac{1}{3\tau(S_1)} \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right)} \quad (1)$$

in which k_B and T represent the Boltzmann constant and the absolute temperature, respectively. The red curve is fitted according to Eq. 1. $\tau(S_1)$ and $\tau(T_1)$ are the decay time of the lowest singlet and triplet excited states, respectively, and ΔE_{ST} is the energy gap between these two states. The fitting curve functionalized by the equation is consistent with the

obtained experimental data of decay time. The parameters obtained are as follows: $\tau(S_1) = 319$ ns, $\tau(T_1) = 37.12$ μs , and $\Delta E_{ST} = 0.097$ eV. Owing to the small ΔE_{ST} , the triplet excitons in T_1 state can be thermally activated and convert to the singlet excitons in the S_1 state at room temperature, and in turn return to the ground state via radiative transition with

TADF emission. This typical TADF mechanism has been observed from Cu(I) complexes and pure organic compounds

consisting of donor-acceptor with small S_1-T_1 energy gaps^[16-18].

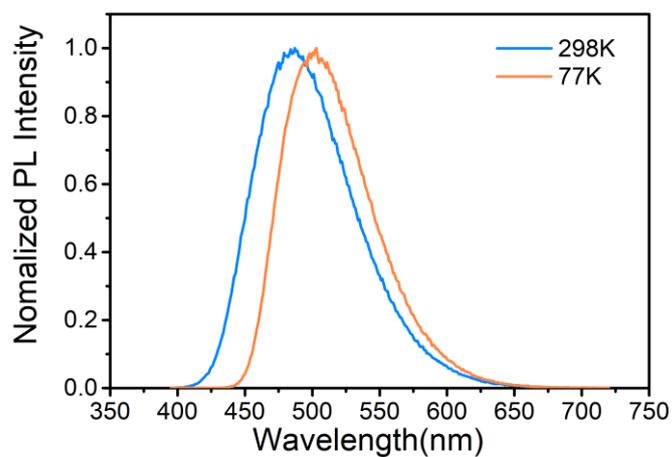


Fig. 4. Emission spectra of $(\text{CuBr})_4(\text{PN})_2$ at 77 and 298 K

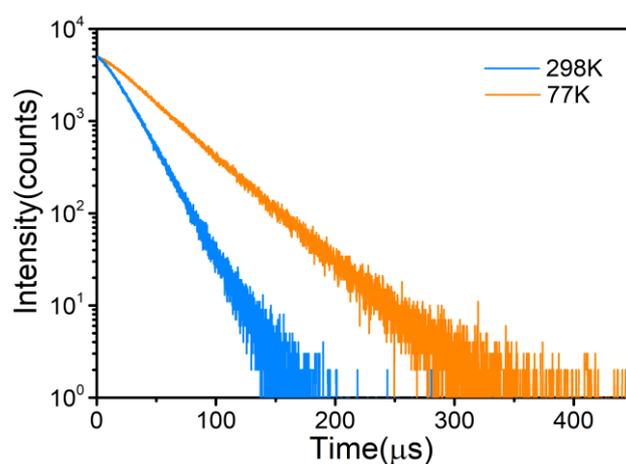


Fig. 5. Transient PL decay curves of $(\text{CuBr})_4(\text{PN})_2$ at 77 and 298 K

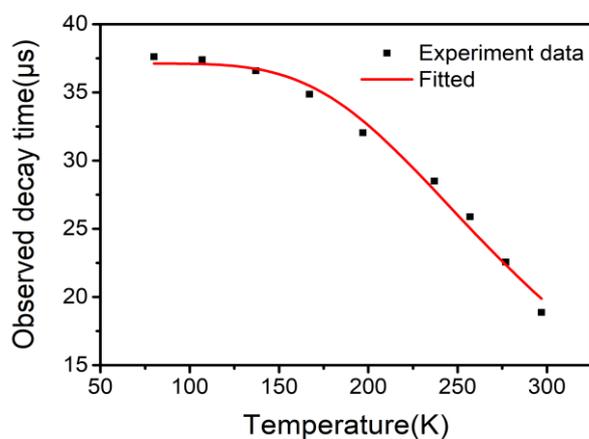


Fig. 6. Temperature dependence of the decay time for complex in the solid state. The black cubes represent experiment data and the red solid line represents a fit curve according to Eq. 1

4 CONCLUSION

In summary, a new tetranuclear cuprous halide cluster chelated by two same PN ligands was designed and synthesized. This complex exhibits intense blue photoluminescence with a PLQY of 43.3% and a lifetime of 19 μ s at room temperature. Theoretical and experimental studies revealed the TADF nature of the blue emission of the investigated complex. Introducing electron-rich substituents

onto the ligand to destabilize the LUMO level has been demonstrated as an effective strategy to tune the emission color to blue region by theoretical predictions and comparative studies. These results may provide a reference for designing efficient cuprous halide materials with blue emission which are required in electroluminescence applications. The application of the investigated complex in electroluminescence devices is under way.

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